PRESERVATION OF HIDES WITH SULFITE. II. A MATCHED SIDE COMPARISON OF LEATHERS FROM HIDES PRESERVED WITH SODIUM SULFITE OR BRINE CURING

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ABSTRACT

A matched side experiment was carried out to corroborate small scale studies (1, 2) on the effectiveness of an acidified sulfite solution** as a short-term preservation system for fresh hides.

One side of each hide was conventionally salt cured and the other was treated with a 20 percent float containing 1.5 percent sodium sulfite and one percent acetic acid (on hide weight). Using six matched sides for each storage period, the sides were held six, 14, and 28 days at ambient temperatures. The leathers prepared from the preserved hides were tested for tensile strength, suitability for lasting, and shrinkage temperature. The preservation was also monitored by using microbial counts and noting the odor of the hides. The leathers made from sides held for all three storage periods were considered commercially acceptable. The results demonstrated that acidified sulfite provides an alternative to salt curing for the short-term preservation of hides. The new method reduces the dissolved solids in tannery effluents, an identified pollution problem caused by the use of salt cured hides. In addition, the reduction of the microbial load in the preserved hides provides more sanitary conditions for hide handling.

INTRODUCTION

The traditional curing of fresh hides with sodium chloride has been recently defined as a pollution problem because it results in high concentrations of dissolved solids in tannery effluents which cannot be removed economically (3, 4). A trend toward the direct use of fresh hides by the tanning industry is also motivated by the fact that the elimination of salt curing is an economic factor in view of the high cost of raw materials and labor (5, 6). Our previous reports have demonstrated methods of short-term and extended short-term preservation

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**WARNING ON SO_2: Caution must be exercised with acid solutions containing Na_2SO_3 because of SO_2 evolution.

of fresh hides (1, 2). Short-term preservation would complement the trend to use fresh hides by allowing more flexible scheduling in the processing of these hides.

The American Leather Chemists Liaison Research Committee has suggested one week as a workable time span for a short-term preservation. Extending the preservation period to seven days would allow time to collect hides over a wider area, time to schedule processing more efficiently, as well as time to hold hides without damage in instances of unscheduled delays in shipping or processing. An added benefit of such a preservation would be maintaining the hides in a more sanitary condition during initial handling.

The purpose of the work was to conduct matched side experiments to corroborate the results of work done on a smaller scale. We stored sides for six, 14, and 28 days to determine the effects of various storage times on the preservation and the leather-making properties of the sides. If the fresh sides could be preserved for 14 and 28 days and made into acceptable leather, then the reliability of the method for a seven-day preservation would be enhanced.

EXPERIMENTAL

Materials and Methods

A total of 18 cowhides was used, six hides for each storage period. Six hides were picked up immediately after slaughter on each of three successive days and the hides were then sided and marked. One half of each side was commercially brined in a cement mixer, using solid sodium chloride and a commercial biocide. The sides taken to our laboratory tannery were tumbled in a stainless steel lined drum at ten r.p.m. for 1.0 hour in a 20 percent float containing 1.5 percent Na_2SO_3, 1.0 percent acetic acid, and 0.03 percent Tergitol 15-S-9†. All ingredient strengths are based on hide weight.

After treatment, two sides from each lot were drained for 0.5 hour by hanging over a horse. The remaining sides were stored with aliquots of the treatment solution. Each side was stored in a separate polyethylene bag and the bags were held in rigid, covered plastic boxes at ambient temperatures.

Finished garment light shoe upper leather was made from sides which were held for six or 28 days. Sides held for 14 days were processed into crust upholstery leather. In all cases the sulfite-acetic acid preserved sides were processed with the tanner's normal fresh hide process and the brined control sides were processed with brined sides. The garment shoe upper leather was processed by H. Swaboda and Sons, Philadelphia, Pa., and the upholstery leather by Chestnut Operating Co., Reading, Pa.

Microbial counts were used as indicative of the preservation of the samples. Each preserved side was sampled at the appropriate times by cutting off small

†Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

pieces from the edges. Three samples were taken, one from the top surface, one from the interior of the folded hide, and one from a part of the side immersed in the residual solution. These pieces weighed approximately 50 to 100 grams each. The pieces were then transferred to a weighed, sterile mason jar, weighed again, and then immersed in 1000 ml. of sterile water. The jars were shaken on a rotary shaker at 200 r.p.m. for 15 minutes. Serial dilutions were made from the wash solutions. Samples from each dilution were plated on standard plate count agar and the plates were counted after 72 hours of incubation at ambient temperature. Three brined sides from each of the six and 28 day stored sides also were sampled for microbial counts. The results for these storage periods are reported as the average of the three bacterial counts made within a storage period.

Our leathers were tested for shrink temperature, tensile strength, and SATRA Grain Crack extension. All samples for testing came from the butt area. The physical test data reported were the average of three values. The tensile strengths were determined by the Official Methods of the ALCA (7). The SATRA Lastometer Mark II was used for the SATRA Grain Crack test. This test followed the Methods of the International Union of Leather Chemists' Societies, where it is called the "Ball Burst Test" (8). An extension at grain crack of seven mm. or more should give a leather which is satisfactory for lasting in most cases. A result which is less than six mm. represents leather that is unsuitable for lasting.

The leathers were also given a subjective evaluation by the commercial tanners for characteristics such as break, appearance, and acceptability.

A number of our matched side pairs were lost because several brined sides could not be positively identified and nine sides were lost in processing.

RESULTS AND DISCUSSION

The microbial counts made on the experimentally treated sides and the brined sides after six, 14, and 28 days of storage are presented in Table I. These counts

TABLE I

MICROBIAL COUNTS ON PRESERVED COWSIDES

Treatment	6 Day (Bact./gm. Hide)	14 Day (Bact./gm. Hide)	28 Day (Bact./gm. Hide)
Sulfite-acetic acid (held with float)	10,000 (4)*	4,600 (4)	14,600 (4)
Sulfite-acetic acid (drained)	1,000 (1)	2,700 (2)	14,100 (2)
Brine cured	15,000,000 (6)	—	900,000 (6)

*Three test pieces were taken for a bacterial count from each side. The number in parenthesis indicates the number of sides in each test.

indicated that the experimental treatment maintained a low bacterial load throughout storage.

The experimental sides stored in the treating solutions through 28 days of storage showed no obvious microbial growth and there was no off odor or noticeable odor of sulfur dioxide. The sides which were drained of excess solution before storage also had a normal appearance and odor after six and 14 days of storage. However, after 28 days, one of the drained sides appeared to have a small spot of microbial growth on the exposed upper hair surface. A scraping of the area was plated and the results indicated it to be bacterial growth. However, the bacterial counts made from the edge sampling of this side did not show high bacterial numbers. The brined control sides showed a comparatively high microbial count at both six and 28 days.

Tensile strengths and SATRA Grain Crack values for finished garment light shoe upper leather prepared from sides preserved for six days are presented in Table II. All leathers, whether made from brined or experimentally preserved sides, gave tensile values above 2000 p.s.i. The SATRA Grain Crack extensions

TABLE II

PHYSICAL TEST DATA* ON GARMENT LIGHT SHOE UPPER LEATHER (FROM SIDES PRESERVED FOR 6 DAYS)

Tensile Strength				SATRA Grain Crack			
Experimental Sides		Brined Sides		Experimental Sides		Brined Sides	
Elongation (%)	Tensile (p.s.i.)	Elongation (%)	Tensile (p.s.i.)	Extension (mm.)	Break Load (kg.)	Extension (mm.)	Break Load (kg.)
52†	2330	51†	2820	9.07†	15	8.56†	12
40†	2240	52†	2240	7.57†	9	8.16†	18
48 (D)	2500	47	2130	8.62 (D)	16	8.74	15
		41	2570			8.51	15
		57	3125			8.58	21

*All samples came from the butt area. Results are the average of three values. Tensile strength was determined parallel to the backbone.

†Indicates that experimental and brined sides are matched.

(D) Drained of excess treatment solution before storage.

were all well above seven mm., a fact that indicates satisfactory grain strength for lasting purposes. Draining the experimentally preserved side before storage did not affect the SATRA or the tensile values of the leather made from these sides.

Crust upholstery leather was made from the sides which were preserved for 14 days. Table III gives the tensile strengths and SATRA Grain Crack values of this leather.

TABLE III

PHYSICAL TEST DATA* ON UPHOLSTERY LEATHER IN THE CRUST
(FROM SIDES PRESERVED FOR 14 DAYS)

Tensile Strength				SATRA Grain Crack			
Experimental Sides		Brined Sides		Experimental Sides		Brined Sides	
Elongation (%)	Tensile (p.s.i.)	Elongation (%)	Tensile (p.s.i.)	Extension (mm.)	Break Load (kg.)	Extension (mm.)	Break Load (kg.)
44 (D)†	1765	31†	1835	8.10 (D)†	32	7.77	23
39†	1910	44†	1850	7.55†	20	7.81	14
42 (D)†	1625	41†	1980	7.54 (D)†	17	7.58	14
35†	2755	41†	2630	7.76†	29	7.69	26
37	2085	46	2295	7.76	23	7.04	18
46	2060	43	1920	8.89	24	7.57	20

*All samples come from the butt area. Results are the average of three values. Tensile strengths were determined parallel to the backbone.

†Indicates that experimental and brined sides are matched.

(D) Drained of excess treatment solution before storage.

The tensile strengths of the treated and control leathers are comparable, although somewhat lower than the samples held for six days. The leather prepared from the drained experimental sides gave the two lowest tensile strength values, a fact that may indicate that draining the treatment solution before storage can affect this property of the leather. The SATRA Grain Crack extensions of all the leathers made from the brined and experimentally treated sides show that all the leathers were satisfactory for lasting purposes. Draining the treatment solution from the sides before storage did not appear to affect this value.

The sides preserved for 28 days were made into finished garment light shoe upper leather and Table IV gives the tensile and SATRA Grain Crack data obtained from these leathers. When the tensile strength of leather made from the experimental sides is compared to that of the brined sides, the treated hides were observed to have tensile strengths consistently lower. The two drained samples again gave the lowest values. When these results were compared to tensile strengths obtained from the same type of leather prepared after only six days of storage, the trend was toward lower tensile strength values for the leather prepared from sides stored for the longer period. This was true whether the leather was made from a brined side or an experimentally preserved side. The SATRA Grain Crack data show all extension values are above seven mm. There is no apparent difference between leathers from brined or experimentally treated sides, nor any effect from draining the treatment solution before storage.

Table V gives the shrink temperatures of the leathers. The data do not show any differences between the leathers made from either the brined or treated sides

TABLE IV

PHYSICAL TEST DATA* ON FINISHED GARMENT LIGHT SHOE UPPER LEATHER

(FROM SIDES PRESERVED FOR 28 DAYS)

Tensile Strength				SATRA Grain Crack			
Experimental Sides		Brined Sides		Experimental Sides		Brined Sides	
Elongation (%)	Tensile (p.s.i.)	Elongation (%)	Tensile (p.s.i.)	Extension (mm.)	Break Load (kg.)	Extension (mm.)	Break Load (kg.)
44 (D)†	1770	50†	2115	8.63 (D)†	18†	8.41	20
50 (D)†	1745	36†	2440	8.81 (D)†	14†	8.99	20
46	1895	50	2140	8.95	19	8.74	23
51	1945	43	2145	8.09	13	8.07	11

*All samples came from the butt area. Results are the average of three values. Tensile strength was determined parallel to the backbone.

†Indicates that experimental and brined sides are matched.

(D) Drained of excess treatment solution before storage.

TABLE V

SHRINK TEMPERATURES OF CRUST LEATHERS (°C.)

6 Days (*a*)		14 Days (*b*)		28 Days (*a*)	
Experimental	Brined	Experimental	Brined	Experimental	Brined
107	105	105 (D)	106	103 (D)	105
104	105	106	107	104 (D)	105
103 (D)	101	106 (D)	107	104	106
	103	110	105	102	
	105	107	105		
		107	107		

(*a*) Finished garment, light shoe upper leather.

(*b*) Upholstery leather in the crust.

(D) Drained of excess treatment solution before storage.

within a storage period. The leathers made from sides held six and 28 days are comparable, and the shrink temperatures do not reflect any effect due to different storage times.

The tanner's comments on the garment light shoe upper leather in the crust stage are as follows: "The leathers made from either the brined or experimentally treated sides which were held for six or 28 days were acceptable. The crust leather made from the sulfite-treated sides had a softer, silkier feel than the leather made from either the brined sides or the normal production leather. It

had good break but there was a tendency for the fat wrinkles to be more prominent than in normal production leather." After finishing, this leather quality was again judged to be within the normal variation in quality for normal production, but the finished leathers made from the 28 day preserved sides were evaluated as better than the leather made from the six day preserved sides.

Two of the sides from a recovered matched pair did show many dull round spots in the neck area. They were not indented but were a lighter colored area against the darker background of the sides. Since they were a matched side pair, this effect was inherent in the hide itself.

The sides preserved for 14 days and made into crust upholstery leather were all judged acceptable. The break was generally tight but the flanks were empty. Cowsides do not have as much hide substance in the flanks as steerhides and splitting into upholstery leather causes this area to be quite thin.

Two sides of this group, one brined and one experimentally treated, had coarse break and were veiny. Since they were a matched side pair, these defects were due to the hide itself rather than to the experimental treatment. Although poor, the sides could be used. One tanner indicated that this leather might be suitable for shoe upper because of its temper and tight break.

SUMMARY

The SATRA Grain extensions for all the leathers which were prepared from our treated sides were 7.0 mm. or more, a fact that indicated they were suitable for lasting. No differences due to the length of time the sides were stored or to the presence or absence of treatment solution when the sides were stored could be determined using this test value.

When the tensile strengths for leather made after six days of storage are compared to those of the leather made after 14 and 28 days of storage, there is a trend to lower values. This is true whether the preservation was with brine or with sulfite and acetic acid. This drop may not be important as long as the tensile values of the leather remain above an acceptable minimum.

Draining the sides of excess treatment solution before storage did not appear to have much effect on preservation. The tensile strengths of the leather prepared from the sides stored 14 and 28 days were the lowest within their respective storage period; however, they were not much lower than the next higher values. After 28 days of storage microbial growth had started on one of the drained sides; however, all the leather made from the drained sides was judged acceptable.

These results show that short-term and extended short-term preservation of up to 28 days is possible using a sulfite-acetic acid solution as a preservation treatment. It is recommended that storage times be kept to not more than one week until more data are available on the effects of longer storage times.

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